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Technical Report on Contract

N6 ONR-269, T. O. III and X

by

J. G. Aston  
Director, Cryogenic Laboratory

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Contribution from the School of Chemistry and Physics of the Pennsylvania State College

## ROTATION IN SOLID MIXTURES OF NEOHEXANE AND CYCLOPENTANE FROM 20°K TO THEIR MELTING POINTS

This research was carried out under Contract N6 Onr-269 (T.O. III and X) of the  
Office of Naval Research

by J. G. Aston, Bouwe Bolger\*, Ralph Trambarulo\*\* and H. Segall

\*Present address: Kamerlingh-Onnes Laboratory, University of Leiden.

\*\*Present address: Physics Department, University of Delaware

### SUMMARY

Studies of the broadening of the proton spin resonance line have been made for solid solutions of neohexane and cyclopentane.

A convenient apparatus for control of temperatures from 10°K to room temperature for such studies is described.

The "complex" of one mole of neohexane with two moles of cyclopentane rotates in the solid state down to 65°K. In solid solutions with cyclopentane in excess of the complex, the complex rotates independently of the cyclopentane down to 66°K. The complex has no effect on the lower rotational transition of the cyclopentane which apparently nucleates.

### INTRODUCTION

The solid-solid and solid-liquid equilibria in the system neohexane-cyclopentane have been fairly exhaustively investigated above 90°K<sup>1</sup>.

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<sup>1</sup>H. L. Fink, M. R. Cines, F. E. Frey and J. G. Aston. J. Am. Chem. Soc. 69, 1501 (1947).

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The phase diagram as obtained from the thermal data is shown in Fig. 1. The pure components each has two transitions of the rotational type. These and the melting point by a curious coincidence are close to the same temperatures for the pair of compounds. It will be shown that the  $\alpha$  to  $\beta$  rotational transitions, while comparable as to their heat

may bear little detailed similarity.

Unfortunately while x-ray studies have been made above the upper transition in both compounds which there show complete freedom of rotation<sup>2</sup>, no measurements were made in the region between the rotational transitions.

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<sup>2</sup>B. Post, R. S. Schwartz and I. Fankuchen, J. Am. Chem. Soc. **73**, 5113 (1951).

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In keeping with the original nomenclature, for both compounds the form stable below the lower transitions will be denoted by  $\alpha$ , that stable between the transitions by  $\beta$  and that stable above the upper transition by  $\gamma$ . There is certainly little rotation for either compound in the  $\alpha$  form. The natures of the rotational motions in the  $\beta$  forms of the two compounds and of the  $\alpha$  to  $\beta$  transitions are open to speculation.

There are two notable features about the condensed phase diagram as obtained from the thermal data. One of these is that there were no thermal transitions above 90°K in the solid for compositions richer in neohexane than corresponding to the "complex" of one neohexane molecule with two cyclopentane molecules. The first solid curve (marked d) in Fig. 1 shows the temperatures of the  $\alpha$  to  $\beta$  transition. The other notable feature is the small variation in equilibrium temperature together with the decreasing heat of the  $\alpha$  to  $\beta$  transition of cyclopentane as neohexane was added. From these it could be inferred that the  $\alpha$  to  $\beta$  rotational transition involved only cyclopentane molecules not in the complex. This conclusion is strikingly verified by the fact that the heat of the transition is proportional to the amount of cyclopentane in excess of the compound. Such an inference implies nucleation<sup>3</sup>. It will take a careful study of the heat capacities below the  $\alpha$  to  $\beta$  transition to tell if there is bulk phase separation.

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<sup>3</sup>R. Smoluchowski, Phase Transformation in Solids, Chap. 5, John Wiley and Sons, New York, (1951).

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Nuclear magnetic resonance has been used to study rotation in the solid state<sup>4 a, b, c</sup>

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<sup>4a</sup>F. Bitter, N. L. Alpert, H. L. Poss, C. G. Lehr and L. T. Linn, Phys. Rev. **71**, 738 (1947).

<sup>4b</sup>N. L. Alpert, Phys. Rev. 72, 637 (1947).

<sup>4c</sup>H. S. Gutowsky and G. E. Pake, J. Chem. Phys. 18, 162 (1950).

The present study by means of nuclear magnetic resonance follows previous methods. It has confirmed all conclusions from the thermal data and added to the knowledge of the extent of rotation in the solid system below the melting point.

#### EXPERIMENTAL

Nuclear Magnetic Resonance Apparatus. - The apparatus is essentially that described by Pound and Knight<sup>5</sup>. It is shown as a block diagram in Fig. 2 which is self-explanatory.

<sup>5</sup>R. V. Pound and W. D. Knight, Rev. Sci. Inst. 21, 219 (1950).

The characteristics of the line were obtained from an oscillograph display with a 30 cps sinusoidal sweep on both the magnetic field and the horizontal axis of the oscillograph. Line widths were measured at half the height of the pattern appearing on the oscillograph face. In such a display the horizontal axis is linear in frequency (or magnetic field strength). This axis was calibrated in kilocycles per second from the positions of sharp lines in the liquid state for various settings of the oscillator frequency which was measured with a BC 221 frequency meter.

Relative intensity in the neighborhood of a transition could be obtained where desired by changing the vertical gain setting of the oscillograph to bring the peak to a previously chosen reference height. For very broad lines or for line shape derivative presentation, the oscillator was turned slowly through resonance by a clock motor and with a very small 280 cps modulation on the magnetic field. The derivative of the line shape is displayed on the recorder through the phase-sensitive lock-in amplifier in the limit of low magnetic modulation.

Magnet. - A permanent magnet with a 2 in. gap between 6 in. pole faces giving a field of 5536 oersted was used. This was manufactured specially by the Indiana Steel Company. By the use of three small iron strips on the raised rim of the pole faces a region of 1 in.<sup>2</sup>

in the middle of the faces was obtained in which the field did not vary by more than  $10^{-2}$  oersted. (The original variation on the same area was about  $40 \times 10^{-2}$  oersted).

Cryostat and Temperature Measurements. - The sample holder (6 cc. capacity), A, (see Fig. 3) was mounted in an evacuated chamber, B, to which small quantities of pure helium could be added for heat conduction. This was fastened to its cover by Woods metal. A copper - constantan thermocouple, C, made from the same spools as the laboratory standard thermocouples S-1 to S-8 passed down through the filling tube, D, with its junction at the bottom<sup>6</sup>. Where the wires passed out of the tube the insulation was removed so that

<sup>6</sup>J. G. Aston, E. Willihnganz and G. H. Messerly, J. Am. Chem. Soc., 57, 1642 (1935).

they could be soldered to caps through which they passed. These caps closed two "cover" tubes sealed onto Pyrex side tubes, E. The samples could be poured in through the filling tube with a suitable funnel. The sample tube was equipped with a constantan heater, F, with current and potential leads so that the assembly could be used as a crude calorimeter of the Nernst type or as a heat leak calorimeter for cooling or warming curves. For this reason, the coil, G, for detecting absorption in the radio region surrounded the sample tube as closely as possible, without actually touching, so as to reduce heat leak by conduction down the heavy copper conductor in the coaxial cable, H. The assembly was supported through a rubber tube seal, by the cap which closed the strip silvered dewar, I. This cap was fitted with tubes for filling with liquid nitrogen or hydrogen, J, and for evacuation and connection to the hydrogen gas holder, K. One filling of liquid hydrogen (2 liters for cooling and filling) lasted for about four hours.

A deviation table, accurate to  $0.10^\circ$  from  $20^\circ\text{K}$  to  $273^\circ\text{K}$ , for the thermocouple was obtained by means of fixed points including the normal boiling point of hydrogen.

Samples. - The cyclopentane was the same sample as used in the thermal studies<sup>1</sup>. The neohexane, kindly supplied by the Phillips Petroleum Company was purified by fractional melting and contained probably no more than 0.3 mole percent purity.

## RESULTS

Line breadths in kcps ( $4.26 \text{ kcps} = 1 \text{ gauss}$ ), obtained from the nuclear resonance along with thermal data previously obtained are given for the pure compounds and mixtures in Table I. Widths below 23 kcps (5.4 gauss) in the solid are considered unusually narrow due to rotation. For convenience, dotted lines a, b, and c on figure 1 connect temperatures corresponding to narrowing of the resonance line between corresponding limits (i.e. relatively sharp changes in line width) which can be ascertained by reference to Table I. It is not implied that these curves represent (other than by pure guess) what is to be expected at unstudied compositions. Because the lines did not change width at definite temperatures, but rather over ranges in temperature, these ranges are indicated by the vertical heights of ellipses drawn for the various concentrations studied. In addition to the curves shown, there was observed a slight (and only slight) narrowing of the lines upon melting. On the neohexane side of the "complex", warming curves were started at  $20^\circ\text{K}$  to be sure that no significant transitions were missed. The curve a, which exists only on the cyclopentane rich side of the "complex", corresponds to further narrowing of an already narrow line. This curve is to be associated with the  $\alpha$  to  $\beta$  transition for cyclopentane found in the thermal data and shown in curve d. The temperature of the  $\alpha$  to  $\beta$  transition is hardly affected by composition. Since its heat depends on the amount of cyclopentane in excess of the complex<sup>1</sup>, only the excess cyclopentane is involved in it. This behavior must result from nucleation. That the  $\alpha$  to  $\beta$  transition of the excess cyclopentane results in narrowing of a line already narrow due to rotation of the compound can be seen from Table I at 79.7 mole percent cyclopentane. At the  $\beta$  to  $\gamma$  transition of cyclopentane the line has become very narrow.

On the neohexane rich side curves b and c (insofar as they are defined by two compositions) change with composition so regularly as to indicate no similar nucleation in neohexane. This is further shown by absence of the curve a. It is quite likely that the pseudo symmetry of the neohexane is the cause of this difference. Curve b extends over the entire diagram with a minimum at 66.7 percent cyclopentane. It corresponds to rotation setting in for the complex. On the cyclopentane side of the complex the nucleated



cyclopentane apparently does not partake. The surprising fact brought out by this study (confirming a conclusion from the thermal data) is the persistence of rotation of the complex found at 66.7 percent cyclopentane down to at least a temperature of 65°K and its ability to lower the  $\alpha$  to  $\beta$  transition of mixtures richer in neohexane. The transition at 65°K found by change in line shape for the compound at 66.7 percent cyclopentane was clearly shown by a flat in the cooling curve associated with heat evolution. Its heat will be measured as part of an investigation now in progress to study its zero point entropy.

For compositions less than 67 percent cyclopentane as well as for pure neohexane line shapes showed hyperfine structure which became resolved at temperatures indicated by the lowest dotted curve, b, in figure 1. Recordings of the line-shape derivatives gave four peaks instead of the two which would be obtained for a line without hyperfine structure. Separations of the outer peaks of the derivatives were about 82 kc. This cannot be attributed to coupling of the protons in  $\text{CH}_3$  groups which give separations of about 40 kc<sup>7</sup>.

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<sup>7</sup>H. S. Gutowsky, G. B. Kistiakowsky, G. E. Pake and E. M. Purcell; J. Chem. Phys. 17, 972 (1949).

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For compositions greater than 67 percent cyclopentane these "wings" were not observed.

Inasmuch as this phenomenon occurs on the neohexane side of the diagram one is tempted to associate this with the tertiary butyl group and/or the ethyl group. For pure cyclopentane the  $\alpha$  to  $\beta$  transition results in no narrowing of the nuclear spin resonance line whereas for pure neohexane the main narrowing occurs at the  $\alpha$  to  $\beta$  transition. Thus it is not likely that the  $\alpha$  to  $\beta$  and  $\beta$  to  $\gamma$  transitions in the two compounds can be paired off logically in any simple fashion.

Acknowledgements. - We wish to thank Mr. H. Segall for help with the measurements and Mr. L. F. Shultz for making the liquid hydrogen. Particularly we wish to thank Mr. F. Malloy for the construction of special dewar vessels and other difficult glass work as well as Mr. C. W. Brouse, Shop Superintendent of the School for the construction of the cryostat.

TABLE I

## Summary of Data for System Cyclopentane - Neohexane

Probable Nature of Transition	Transition Temperature °K from Heat Capacity	Trans. in nucl. res. °K	Line width in Kcps
<u>Cyclopentane</u>			
rot. tr. $\alpha \rightarrow \beta$	122.2	not found	not found
rot. tr. $\beta \rightarrow \gamma$	138.1	138.1	64.9 to 6.6
?	not found	152.2	6.6 to 5.5
$\gamma$ to liquid	179.7	179.7	4.8 to 4.4
<u>79.7 mole percent Cyclopentane</u>			
rot. tr.	---	65	50 to 10
rot. tr.	---	101.5 - 105	10 to 7
rot. tr. $\alpha \rightarrow \beta$	121.3	gradual tr. from 121 to 128.5	7.1 to 3.5
rot. tr. $\beta \rightarrow \gamma$	128.0	---	3.5
$\gamma$ to liquid	128.2 - 131.3	---	3.5
<u>66.7 mole percent Cyclopentane (Complex)</u>			
rot. tr.	---	65	50.5 to 11
melting	136.5 - 137.7	130 - 141	11 to 3.5
<u>48.8 mole percent Cyclopentane</u>			
rot. tr.	---	66 - 70	30 to 23
---	---	gradually from 70 - 126	23 to 11
<u>7.1 mole percent Cyclopentane</u>			
rot. tr.	---	108 - 115	25 - 10
---	---	gradually from 115 - 153	10 - 1.7
melting	149.5 - 152.8	---	1.7
<u>Neohexane</u>			
?	---	range 102 - 110	82 - 37
rot. tr. $\alpha \rightarrow \beta$	126.81	range 120 - 128	approximately 37 - 10
rot. tr. $\beta \rightarrow \gamma$	140.88	gradually from	
$\gamma$ to liquid	174.16	128 - 174	10 - 1.7

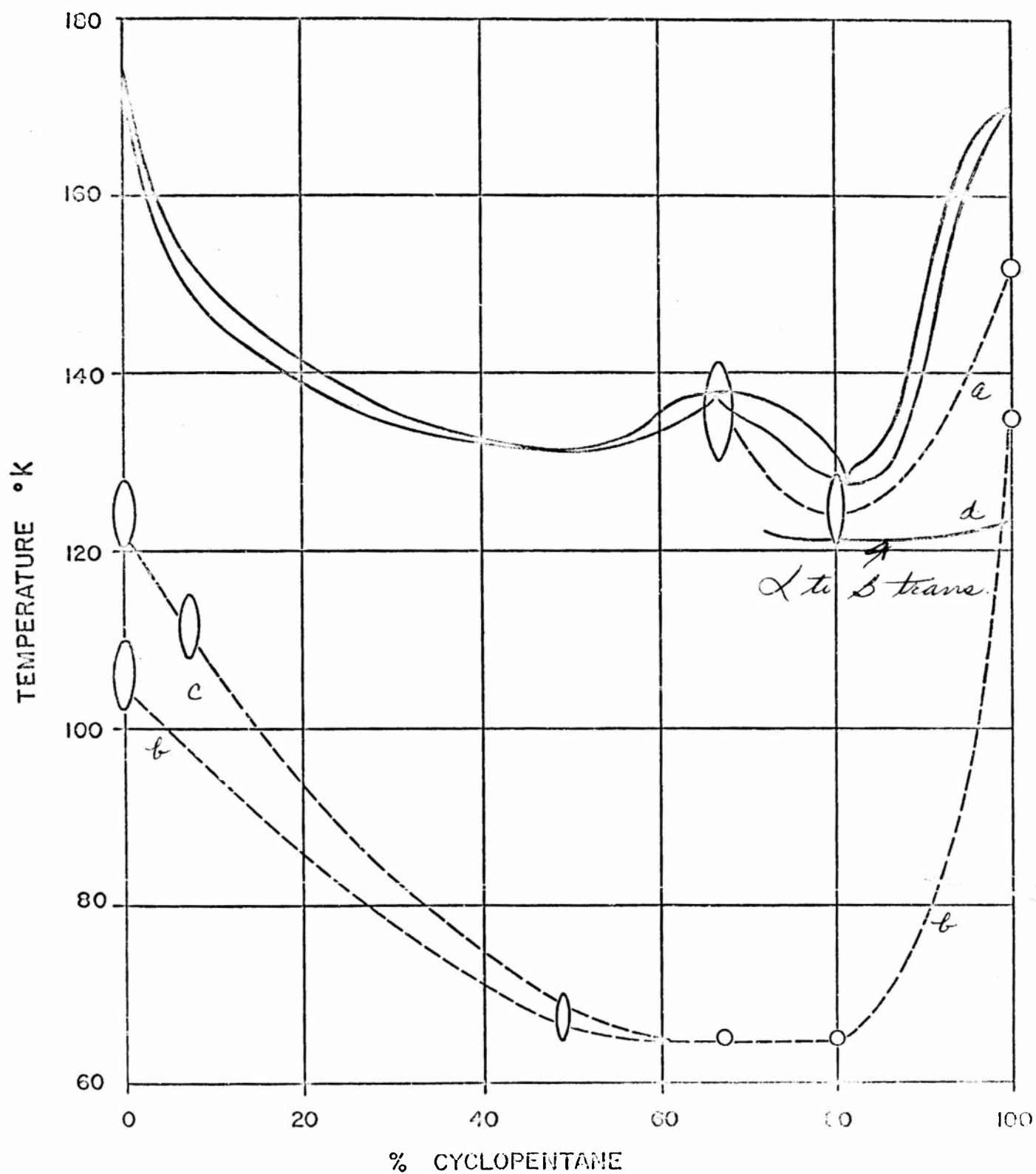


Fig. I Neopentane-Cyclopentane Condensed Phase Changes

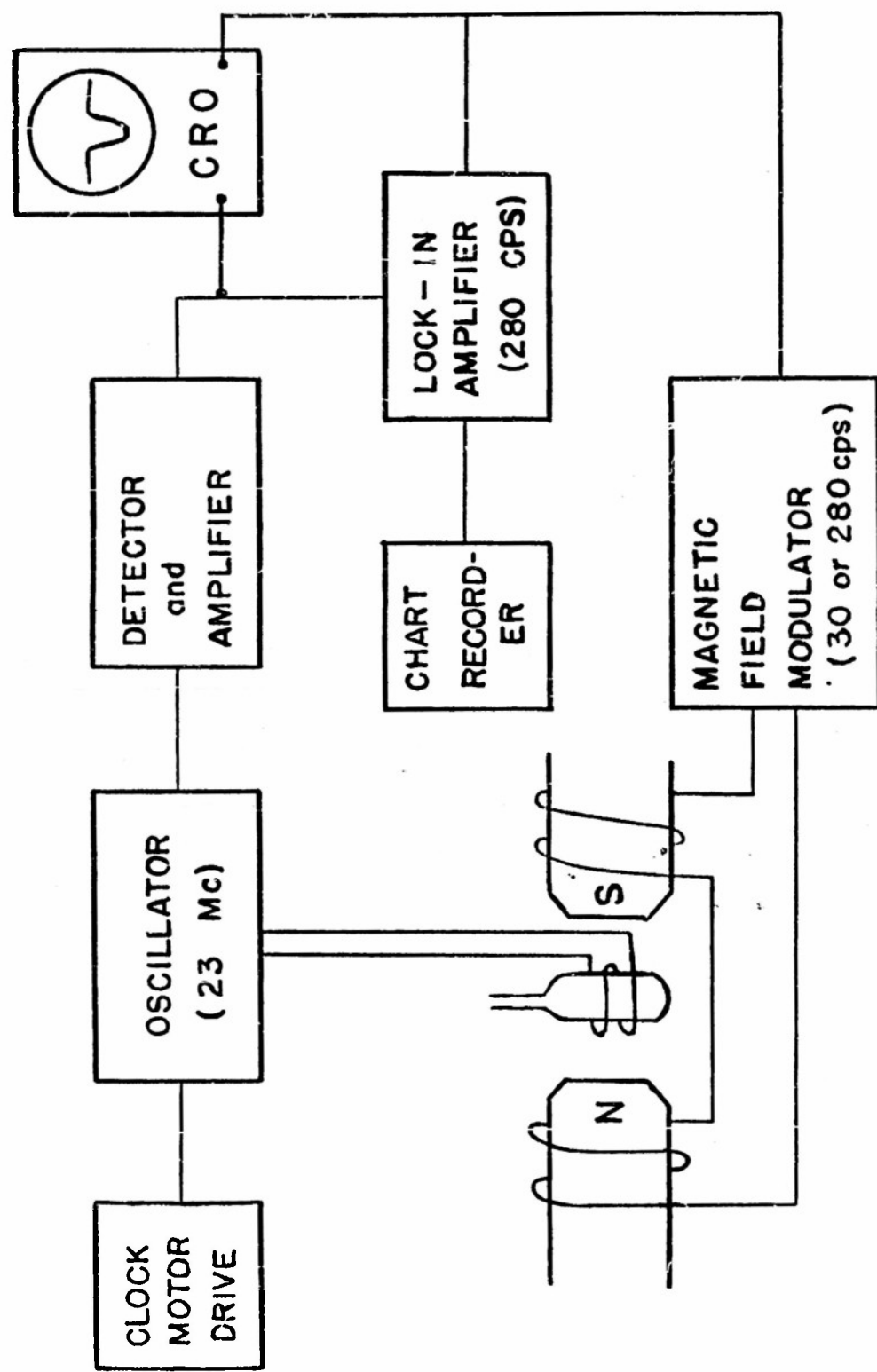


Fig. 2. Nuclear Recorder Assembly

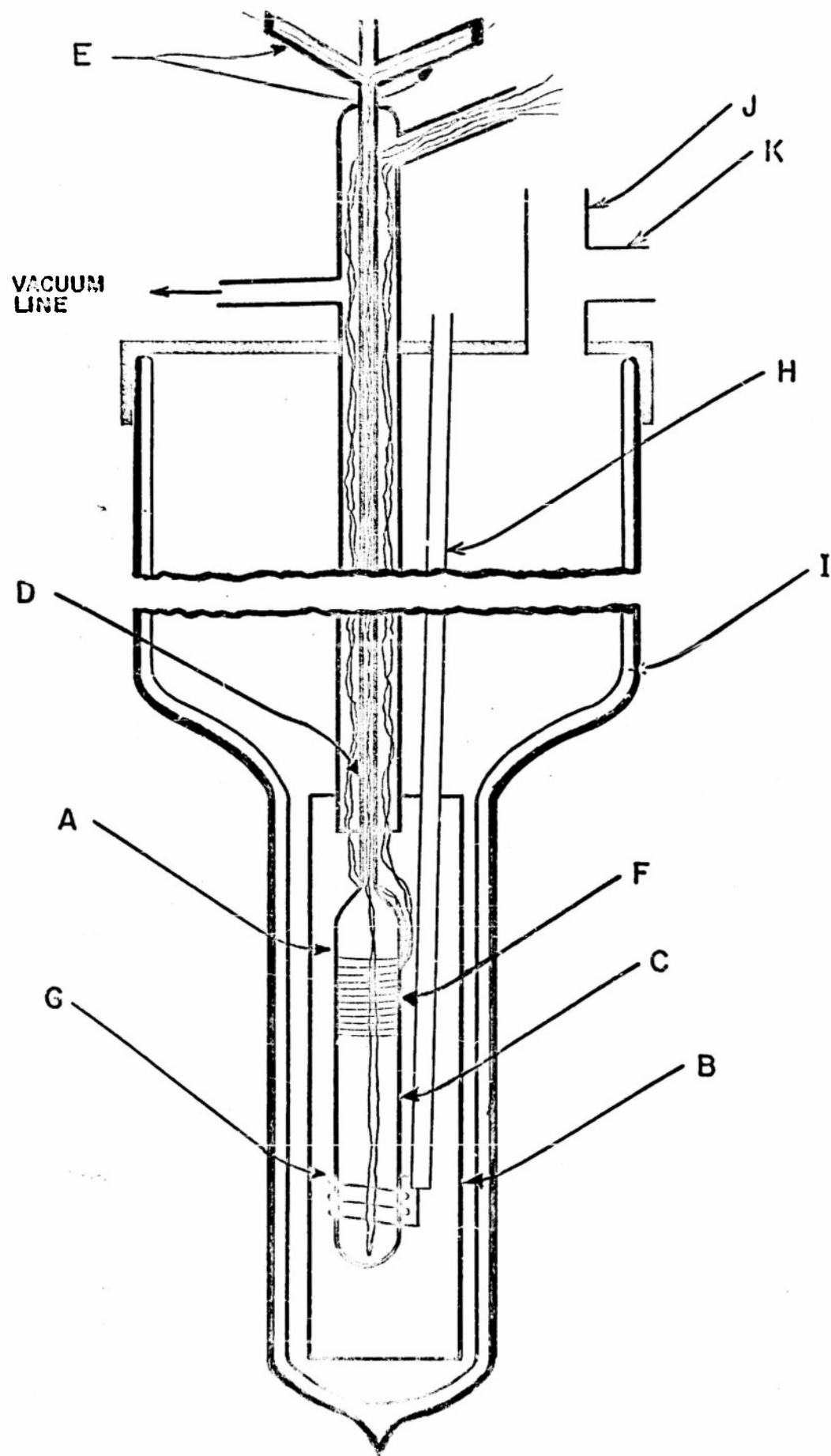


Fig. 1. Cryostat for C<sup>13</sup> for Nuclear Resonance.